

RECENT EXPERIMENTS ON THE CRYSTALLISATION OF MINERALS.

ALTHOUGH the crystallisation of alloys and of minerals must in its nature be essentially similar to that of the more ordinary solutions handled in the laboratory, the ranges of temperature and pressure involved are so far different as to make any experimental study a matter of considerable difficulty. In the case of the metallic alloys, the difficulties incident on the production and measurement of high temperatures have in recent years been overcome by the use of platinum-resistance thermometers, as in the investigation of the copper-tin alloys by Heycock and Neville, or by the use of thermal-junctions of platinum with a platinum alloy, as used so effectively by Roberts-Austen and his colleagues in the work of the Alloys Research Committee. As a result of these investigations, the conditions under which the different constituents separate from a liquid alloy, and the changes which occur as the solid ingot cools, are as fully known as the conditions which determine the separation of ice or salt from an aqueous salt solution.

The study of the crystallisation of an igneous mineral from a liquid magma has proved to be a task of very much greater difficulty. The temperatures of crystallisation are much higher, and frequently lie above the melting temperature of platinum; the minerals to be examined are not easily obtained in a pure state; they are poor conductors of heat and—perhaps the most serious difficulty of all—many of the minerals are so viscous when first melted that several minutes elapse before even the corners of the crystals become rounded; conversely, the melted materials often cool to a glassy mass, and only reluctantly develop a crystalline structure. Difficulties such as these render almost inoperative the methods that have proved so effective in the study of metallic alloys, but new weapons have been provided by the perfecting of the radiation pyrometer as an exact method for the measurement of high temperatures, and by the commercial production of iridium melting at a temperature at least 600° above the melting point of platinum.

A quantitative study of the crystallisation of the lime-silica series of minerals has recently been published by Messrs. A. L. Day and Shepherd, of the Geophysical Laboratory of the Carnegie Institution of Washington (*Journ. Amer. Chem. Soc.*, xxviii., pp. 1089-1114, September, 1906). The results they have obtained are so far in advance of anything that has previously been accomplished as to mark the opening of a new period in the development of experimental mineralogy.

Dealing first with the two pure substances from which this series of minerals is derived, it may be noted that lime melts at so high a temperature that it is not yet possible to make a satisfactory determination of the melting point; measurements can only be made with mixtures containing at least 20 per cent. of silica, and even these melt at temperatures ranging from 1400° to well over 2000° C. The melting point of silica lies below that of platinum, but the melting is so slow that when a charge of quartz was heated in an iridium crucible in an iridium tube-furnace to the melting point of platinum (1700°) the grains did not coalesce, although they became tightly sintered together. Incipient melting could, however, be detected at a temperature nearly 100° lower, and the melting point is fixed by the authors at 1600° C.

Silica is a dimorphous compound, the two mineral varieties being known as quartz and tridymite. At temperatures above 1000° both quartz and amorphous silica change to tridymite. This is, therefore, the form which is stable at the melting point, and the melting temperature of silica is thus properly the melting temperature of tridymite, and not of quartz, as is commonly described. Occasionally by rapid heating quartz can be partially melted without inverting to tridymite, but it would hardly be possible by any known method to determine a separate melting point for unchanged quartz.

The converse change from tridymite to quartz is less easily observed. In presence of a catalyst, such as sodium tungstate, vanadic acid, or a mixture of potassium and lithium chlorides, amorphous silica was found to crystallise to quartz below 760° , and to tridymite above 800° ; by

heating for five or six days the direct change of quartz to tridymite was proved at 800° , and from tridymite to quartz at 750° . The change is therefore reversible, and there is a true inversion point at about 800° C.

The melting-point curve for mixtures of lime and silica was explored by heating mixtures of definite composition, well mixed by grinding and repeated melting, on a platinum or (for higher temperatures) iridium strip, and noting the order of fusion. In this way two maxima and three minima were found, and these were subsequently investigated in such a way as to determine the exact composition and temperature at which each occurs. The maxima at 48 per cent. and 65 per cent. CaO correspond with the composition of the metasilicate CaSiO_3 and the orthosilicate CaSiO_4 , but no indication could be obtained of the separation from the melt of the compounds $2\text{CaO} \cdot \text{SiO}_2$ or $3\text{CaO} \cdot \text{SiO}_2$, or of the silicate $4\text{CaO} \cdot 3\text{SiO}_2$ analogous to the mineral akermanite.

Both the metasilicate and the orthosilicate are poly-

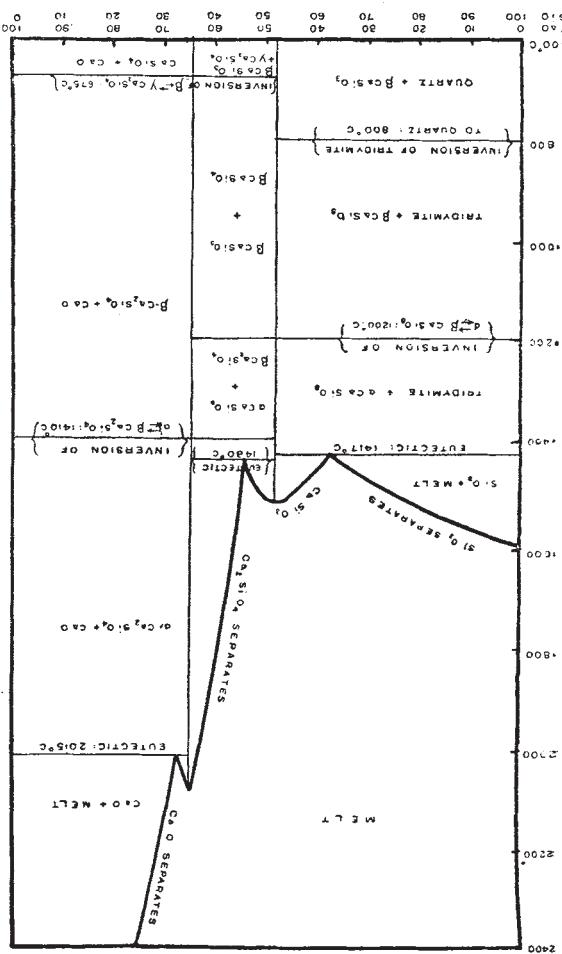


FIG. 1.

morphous. The metasilicate crystallises at 1512° in a pseudo-hexagonal form, and inverts at 1200° to a form identical with the mineral wollastonite. The orthosilicate crystallises at 2080° in a monoclinic α -form of density 3.27, and inverts at 1410° to an orthorhombic β -form of density 3.28, and again at 675° to a monoclinic γ -form of density 2.97.¹ The latter change involves an expansion of 10 per cent. in the volume of the substance, and is thus responsible for the disintegration or "dusting" of the orthosilicate and all mixtures containing more than 51 per

¹ It is unfortunate that the authors have reversed the convention which obtains in the case of iron, whereby the γ -form is that which is stable at the highest temperatures, and the α -form that which is stable at atmospheric temperatures.

cent. CaO. The orthosilicate is readily attacked by water, which dissolves out the lime in large quantities; this is probably the reason why it is not found as a natural mineral.

The three eutectics are:—(1) tridymite+metasilicate, 37 per cent. CaO, 1417° ; (2) metasilicate+orthosilicate, 54 per cent. CaO, 1430° ; (3) orthosilicate+lime, $67\frac{1}{2}$ per cent. CaO, 2015° .

Although the melting point of lime is unknown, the authors have been able to plot a complete diagram of the different equilibria that may occur in this series of compounds (Fig. 1). The importance of such an achievement can scarcely be overestimated, and there can be little doubt that it will play as important a part in the development of experimental mineralogy as Roozeboom's classical diagram for the iron-carbon steels has done in modern metallurgy.

T. M. LOWRY.

CHARACTER AND CAUSE OF SUN-SPOT SPECTRA.¹

IT is now just forty years since the selective widening of Fraunhoferian lines in sun-spot spectra was first observed by Sir Norman Lockyer. Since then various papers relating to the same subject have been published by Sir Norman Lockyer, Prof. Young, and—more recently—Dr. Mitchell and Prof. Hale.

The authors of the present paper state at the outset that in considering the chief features of sun-spot spectra, three points especially attract attention:—

(1) The fact that certain lines in the spectrum of a given element are strengthened, others are weakened, the remainder being unaffected.

(2) The occurrence of the strengthened lines in the visible spectrum only; none appear in the ultra-violet.

(3) The relatively great intensity of the continuous background of the spot spectra in the less refrangible region.

From what is known of laboratory spectra taken under varying temperature conditions, the following facts accrue:—

(1) That in passing from a high temperature to a lower one, certain lines are relatively strengthened, some are unaffected, and others are diminished in intensity.

(2) That such a reduction of temperature is accompanied by an increase in the relative intensity of the less refrangible lines, and a shift of the maximum of a continuous spectrum towards the red.

The general correspondence of these two groups of facts led the authors to seek for an explanation of the spectrum of sun-spots, on the hypothesis that the metallic vapours within the spots have a temperature lower than that of the photosphere.

Photographs of spot spectra, made with the Snow telescope and a Littrow spectrograph of 18 feet (5.5 m.) focal length, and showing a great number of affected lines, were available for the investigation. The range of spectrum covered by these photographs is from D to H β . Supplementary photographs of the spectra of recent large spots, extending from A in the red to the ultra-violet, have been obtained by Mr. Ellerman.

The laboratory work began with a study of iron and other metals in a synchronous rotating arc, designed and constructed by Prof. Crew, but as the necessary photographs involved undesirably long exposures this was not continued. It occurred to Mr. Gale to try the effect of varying the current strength in an ordinary 110-volt direct-current arc, the difference of potential between the poles being kept approximately constant. Photographs were taken, with currents of 30 amperes and 2 amperes, of the spectra of iron, titanium, vanadium, chromium, manganese, calcium, and other metals characteristic of sun-spots. As the work progressed, a correspondence was noted between the enhanced lines (lines stronger in spark than in arc) and those weakened in sun-spots. To get further light on this, photographs were taken of the spectra

of the same elements in the discharge of a 600-watt transformer, giving about 6000 volts at the secondary terminals. A condenser was used in the discharge circuit, and the potential was increased by an auxiliary air spark in series with the observed spark, both being exposed to a strong blast of air from an electric fan. Under these conditions the enhanced lines of the spark are well shown.

The instrument used to obtain the majority of the laboratory photographs was a grating spectroscope in the Littrow form of 13 feet (3.96 m.) focal length. The Michelson grating has 700 lines to the millimetre. In taking the comparison photographs of strong- and weak-arc spectra, two of the strong-arc spectra, with varying exposures, were generally placed on each side of the weak-arc spectrum. From the four different strong-arc exposures thus obtained that one was selected which was most nearly comparable in general strength with the weak-arc spectrum. In some cases the spark spectrum was added, adjoining the weak-arc spectrum, with the strong-arc spectra arranged as before.

Tables are given in the paper which contain the results of a study of the elements titanium, vanadium, iron, chromium, and manganese for the region extending from the ultra-violet to $\lambda 5800$. The tables include all the lines which are affected prominently, and which, being strengthened or weakened in spots, or in spark or weak arc as compared with strong arc, are of special importance in the investigation.

In discussing the behaviour of the lines of the elements mentioned, the investigation is divided into two parts, the relation of the weak arc to the strong arc, and of the arc to the spark. Two sets of tables are therefore given. The first shows the wave-lengths of all the lines which are much affected in spots, the amount by which they are affected, their behaviour in the weak as compared with the strong arc, and in the spark as compared with the weak arc. The second set of tables gives a comparison of the intensities of the lines of the same elements which are considerably enhanced in the spark, with their intensities in the weak arc. The majority of these which occur in the less refrangible part of the spectrum are weakened in spots, and such lines therefore appear in both sets of tables. As, however, most of the strongly enhanced spark lines occur in the violet and ultra-violet—where the spot lines seem to have the same intensity as the Fraunhoferian lines—dependent lists of these lines have been added, since the evidence afforded by them as to the relation of spark to weak arc is extremely important.

The authors summarise some of the results accruing from the investigation as follows:—

(1) More than 90 per cent. of the lines in the tables which are strengthened in sun-spots are found to be strengthened in passing from a 30-ampere arc to a 2-ampere arc.

(2) More than 90 per cent. of the lines shown by the tables to be weakened in sun-spots are weakened or absent in the 2-ampere arc.

(3) More than 90 per cent. of all the enhanced lines included in the tables are weakened or absent in the 2-ampere arc.

(4) In a list selected at random of 152 lines which are not spot lines, no cases were found of lines strengthened in the low-current arc.

In discussing the temperature hypothesis as the probable explanation of the observed phenomena, some of the points made are:—

(1) Waidner and Burgess's investigation of the temperature of the arc showed that the temperature of the crater was reduced 70° when the current was reduced from 30 to 15 amperes. As the relative intensities of the lines undergo no material change in passing from 30 to 15 amperes, while the change from 30 to 2 amperes is very pronounced, the temperature of the crater is probably considerably reduced at 2 amperes.

(2) Since the enhanced lines of the spark diminish in intensity in the 30-ampere arc, and are still further reduced in the 2-ampere arc, no explanation hitherto advanced to account for these lines appears adequate in the present case, unless it be the explanation based on change of temperature.

¹ Abstract of an advance proof from Mount Wilson Solar Observatory of a "Preliminary Paper on the Cause of the Characteristic Phenomena of Sun-spot Spectra." ("Contributions from the Solar Observatory," No. 11.) By George E. Hale, Walter S. Adams and Henry G. Gale. The paper is to be published in a future number of the *Astrophysical Journal*.